Application Serial No.: 10/080,555

Inventor(s): ARCELLA et al.

**Attorney Docket No.: 108910-00054** 

**AMENDMENTS TO THE CLAIMS:** 

Please amend the claims as follows:

1. (Original) Porous hydrophilic membranes comprising a porous inert support

on which an ionomer is deposited, said membranes being characterized in that

they have an ionic conductivity in electrochemical cells and a water permeability

higher than 1 l/(h.m<sup>2</sup>.Atm); the ionomer being under amorphous form and having

the hydrophilic group in the acid form.

2. (Original) Membranes according to claim 1, having pores partially or totally

occluded to gases.

3. (Previously Presented) Membranes having pores totally occluded to gases

according to claim 1, containing an ionomer amount higher than about 30% by

weight.

4. (Previously Presented) Membranes having pores partially occluded to gases

according to claim 1, containing an ionomer amount lower than about 20% by

weight.

5. (Previously Presented) Membranes according to claim 1, wherein the porous

support is formed by (per)fluoropolymers, preferably PTFE, still more preferably

bistretched PTFE.

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6. (Currently Amended) Membranes according to claim 1, wherein the ionomers are (per)fluorinated polymers and they <u>optionally preferably</u> have SO<sub>3</sub>H and/or - COOH, <u>and/or preferably</u> SO<sub>3</sub>H, functionality, and an equivalent weight such as to result amorphous.

- 7. (Currently Amended) Membranes according to claim 6, wherein the ionomers comprise:
  - (A) monomeric <u>unites units</u> deriving from one or more fluorinated monomers containing at least one ethylene unsaturation;
  - (B) fluorinated monomeric unites units containing functional groups transformable into hydrophilic groups preferably –SO<sub>2</sub>F and/or COOR, COF, wherein R is a C<sub>1</sub>-C<sub>20</sub> alkyl radical or a C<sub>6</sub>-C<sub>20</sub> aryl radical, in such an amount to give the above equivalent weight, the functional groups being converted into hydrophilic groups, or preferably into –SO<sub>3</sub>H and/or –COOH groups in the final membrane if the functional groups were –SO<sub>2</sub>F and/or –COOR, -COF.
- 8. (Currently Amended) Membranes according to claim 7, wherein the fluorinated monomers of type (A) are selected from the following:
  - vinylidene fluoride (VDF);
  - C<sub>2</sub>-C<sub>8</sub> perfluoroolefins, preferably or tetrafluoroethylene (TFE);
  - C<sub>2</sub>-C<sub>8</sub> chloro- and/or bromo- and/or iodo-fluoroolefins, such as and/
     or chlorotrifluoroethylene (CTFE) and/or bromotrifluoroethylene;

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- CF<sub>2</sub>=CFOR<sub>f</sub> (per) fluoroalkylvinylethers (PAVE), wherein R<sub>f</sub> is a
   C<sub>1</sub>-C<sub>6</sub> (per) fluoroalkyl, for example or trifluoromethyl,
   bromodifluoromethyl, or pentafluoropropyl;
- CF<sub>2</sub>=CFOX perfluoro-oxyalkylvinylethers, wherein X is a C<sub>1</sub>-C<sub>12</sub>
   perfluoro-oxyalkyl having one or more ether groups, or for example
   perfluoro-2-propoxy-propyl.
- 9. (Previously Presented) Membranes according to claim 7, wherein the fluorinated monomers of type (B) are selected from the following:
  - $F_2C=CF-O-CF_2-CF_2-SO_2F$ ;
  - $F_2C=CF-O-[CF_2-CXF-O]_n-CF_2-CF_2-SO_2F$ wherein X = Cl, F or  $CF_3$ ; n = 1-10;
  - F<sub>2</sub>C=CF-O-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>2</sub>F
  - F<sub>2</sub>C=CF-Ar-SO<sub>2</sub>F wherein Ar is an aryl ring;
  - F<sub>2</sub>C=CF-O-CF<sub>2</sub>-CF<sub>2</sub>-COF
  - $F_2C=CF-O-[CF_2-CXF-O]_n-CF_2-CFX-COF$ wherein X = Cl, F or  $CF_3$ ; n = 1-10.
- 10. (Previously Presented) Membranes according to claim 1, wherein the ionomers contain from 0.01 to 5% by moles of monomeric units deriving from a bis-olefin of formula:

$$R_1R_2 C = CH - (CF_2)_m - CH = CR_5R_6$$
 (I) wherein:

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m = 2-10, preferably 4-8;

R<sub>1</sub>, R<sub>2</sub>, R<sub>5</sub>, R<sub>6</sub>, equal to or different from each other, are H or C<sub>1</sub>-C<sub>5</sub> alkyl groups.

- 11. (Previously Presented) Membranes according to claim 1, wherein the ionomers comprise:
  - monomeric units deriving from TFE;
  - monomeric units deriving from CF<sub>2</sub>=CF-O-CF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F;
  - monomeric units deriving from the bis-olefin of formula (I);
  - iodine atoms in end position.
- 12. (Previously Presented) Membranes according to claim 1, wherein the amorphous ionomer shows a substantial absence of crystallinity.
- 13. (Currently Amended) Membranes according to claim 1, wherein the amorphous ionomer has a residual crystallinity lower than 5%, preferably lower than 1%.
- 14. (Previously Presented) Membranes according to claim 1, wherein the (per)fluorinated ionomers are crosslinked.

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15. (Previously Presented) Membranes according to claim 1, containing one or more amorphous or crystalline (per)fluoropolymers, the amorphous ones being different from the ionomer used in the membrane.

- 16. (Original) Membranes according to claim 15, wherein the (per) fluoropolymers are of crystalline ionomeric type.
- 17. (Currently Amended) Use of the membranes according to claim 1 in electrochemical Electrochemical cells operated by the membranes of claim 1.
- 18. (Currently Amended) Use of the membranes according to claim 17 for fuel Fuel cells operated by the membranes of claim 1.
- 19. (Currently Amended) Use of the membranes according to claim 4, wherein the fuel cells are used and an Fuel cells according to claim 18, wherein the membranes have pores partially occluded to gases, and certain ionomer amount lower than about 20% by weight, and wherein the air pressure is used at the cathode side is higher than that of the hydrogen at the anode side, the fed hydrogen coming from reforming and therefore containing CO.
- 20. (Currently Amended) A process for preparing hydrophilic porous membranes according to claim 1, comprising a porous support formed by a (per)fluorinated polymer, and amorphous (per)fluorinated ionomers containing

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hydrophilic groups, preferably having a -SO<sub>3</sub>H or -COOH functionality, said process comprising the following steps:

- impregnation of the porous support formed by the (per)fluorinated a) polymer, with a (per)fluorinated ionomer having hydrolysable functions, preferably -SO<sub>2</sub>F, -COOR, -COF, wherein R is a C<sub>1</sub>-C<sub>20</sub> alkyl radical or a C<sub>6</sub>-C<sub>20</sub> aryl radical, using a solution of the ionomeric compound in fluorinated organic solvent at a concentration in the range 1-20% by weight, preferably 4-20% by weight until obtaining a membrane having the pores substantially filled by the ionomeric solution, the impregnation is carried out at temperatures between the room temperature and 120°C, preferably between 15°C and 40°C; the so impregnated membrane is subjected to thermal treatment at temperatures from 50° to 200°C, preferably from 120° to 160°C until substantial removal of the solvent and obtainment of a substantially transparent membrane, optionally step a) is repeated until the membrane appears substantially transparent;
- b) treatment of the membrane obtained in a) with inorganic strong,

  optionally preferably aqueous, alkalis, i.e. or bases which are

  completely dissociated in water, to obtain the conversion of the

  functional groups into hydrophilic groups, preferably optionally from

  -SO<sub>2</sub>F into -SO<sub>3</sub>, and of the -COOR, -COF groups into -COO

  groups;

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c) treatment of the membrane obtained in b) with inorganic strong acids, i.e. or acids which are completely dissociated in aqueous solution, obtaining the (per)fluorinated ionomer in acid hydrophilic form;

- d) optionally treatment with water at temperatures in the range 50°C 100°C, in case repeated, until removal of the ionomer in excess and neutral pH of the washing waters.
- 21. (Currently Amended) A process according to claim 20, wherein in step a) the solvent has a boiling point at room pressure lower than 180°C, preferably lower than 120°C.
- 22. (Previously Presented) A process according to claim 20, wherein in step b) the used strong alkalis are the hydroxides of the Group la metals.
- 23. (Previously Presented) A process according to claim 20, wherein at the end of step b) washings with water are carried out until a neutral pH of the washing waters is obtained.
- 24. (Previously Presented) A process according to claim 20, wherein the ionomer is crosslinked by adding to the impregnation solution a) crosslinking agents.

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25. (Original) A process according to claim 24, wherein crosslinking takes place by adding peroxides to the impregnation solution and operating at temperatures from 100 to 300°C.

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